New Trends in the Chemical Pretreatment of Metal Surfaces

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Summary: The driving forces for the development of new chemical pretreatment products are both the need for more environmentally compatible processes and improved productivity at the customer. The first trend is met by introducing easily biodegradable surfactants, by avoiding waste and waste water by closed loop pretreatment systems and by substituting hazardous chemicals such as chromates. In the second trend, pretreatment steps are transferred from part lines upstream to the coil lines of sheet metal manufacturers thereby reducing assembling, and painting costs in automotive and white goods industries as well as in architectural application.

Introduction

Chemical pretreatment, although it is necessary within a production process, is in many cases an unliked part of the assembly line. It does not contribute to the outside appearance of the product and therefore cannot be used as a marketing argument. In addition, it often is hot, humid, produces waste and is a frequent cause of failures. Chemical pretreatment is, however, essential for the quality of the product because it fulfills the following tasks:

- it completely removes all residues from earlier production steps such as oils, fats, greases, sputter particles and grinding dust;
- in provides the so-called water break free surface;
- it constitutes a reprodusible and well defined surface condition capable of supporting all subsequent coating operations;
- it builds up a first coating layer usually called „conversion coating“ which is essential for corrosion protection and paint adhesion.

This dilemma of being unwanted but necessary at the same time gives rise to the trends in chemical pretreatment we encounter at present: On the one hand, customers ask for environmentally compatible processes to improve their workers safety by avoiding poisonous chemicals and to reduce energy consumption and wastes to meet regulations. On the other

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hand, we observe a trend to transfer pretreatment steps from part lines to the sheet metal manufactures. Thus, precoated substrates are getting more and more in use thereby improving quality standards and reducing assembly costs.

Thus, pretreatment processes presently introduced in the market or upcoming as the next generation will at the same time reduce environmental risks and improve productivity.

Cleaning

The cleaning stage of a pretreatment line has to remove completely all oils and greases and to condition the surface for all subsequent pretreatment steps. Although, the use of biodegradable surfactants and bath maintenance procedures are state-of-the-art, a new situation has come up by the demand of the EU to introduce socalled „easily biodegradable surfactants“ until 2004. These surfactants have to meet the OECD 301 regulation saying that 60 % of the surfactant has to be decomposed into CO_2 within 28 days. The goal is achieved by the development of a new generation of surfactants with a narrow range of EO groups. Fig. 1 shows EO distribution of both „old“ and „new“ surfactants.

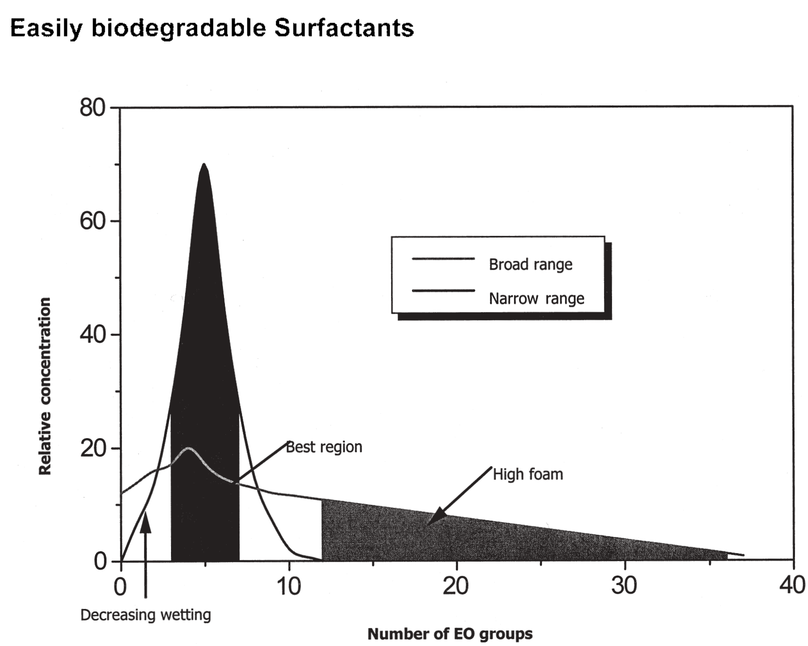


Figure 1.

These new raw materials result in

- better biodegradability,
- significantly better cleaning ability,
- less foaming even near to the cloud point.

Since synthesis of these new surfactants is more complicated, raw material costs are slightly higher which is partly overcome by better efficiency. But as a general rule it turns out that protection of the environment is not for free.

Heavy Metal Free Processes

The discussion carcinogenic chromates is more than ten years old and on one hand in some industries such as the European automotive industry chromates are probably going to be completely banned in 2003 due to the European Directive “End of life vehicle”. For the passivation of zinc and the pretreatment of Aluminium, on the other hand chromic acid treatment still is standard.

As an alternative to yellow chromating of aluminium especially for architectural applications, a new process has been developed that is based on cerium chemistry. It has the interesting feature that it provides a yellow surface which is almost identical to the colour obtained by yellow chromating. Thus, the cerium treatment allows for the same easy quality inspection as the chromate: a uniform yellow coloured surface shows that the process is under control. Fig. 2 provides some test results indicating that the Cerate process has comparable performance to chromate coatings under paint. It must be stated, that bare corrosion protection is not as good as with the chromate coating, which means that Cerate technology is intended to be a pretreatment prior to paint. The customer can use the process in his existing chromating dip line with minor adjustments.

But it is not the chromate ion alone that is under discussion. Nickel compounds are rated as being possibly carcinogenic and other heavy metals give also rise to concern, if only in the waste water treatment system. Thus there is a tendency to avoid heavy metals completely if possible.

As a fist product of this kind we have recently introduced the so-called SAM-technology into the market. It again can be used on aluminium surfaces as a pretreatment prior to painting. The conversion coating in this case consists of monomolecular layer of self assembly molecules. With their head groups, the molecules chemisorb to the hydrated metal oxide layer whereas the tail group is bound to the paint. Thus, we achieve excellent paint adhesion and at the same time very good corrosion protection (Fig. 3). Reason for the corrosion resistance of the layer is the first densely packed layer of molecules which consist beside their end groups of alkane chains which cause the layer itself to be hydrophobic. Thus the layer immediately in contact with the metal acts as a barrier against the diffusion of water and ions.

Figure 2. Cerate Process
Treatment: Cerate pretreatment under Polyester Powder Paint (Herberts Al-88-9010)

Test results	Cerate-Treatment	Chromating-Treatment
Filiform Test, 1008 h (DIN EN 3665)	U < 1	U < 1
Salt Spray Test CASS, 240 h (DIN 50021	U 0	U 0
Salt Spray Test ESS, 480 h (DIN 50 021)	U 0	U 0
Humidity Test KK, 240 h (DIN 50017)	Gt 0	Gt 0

Figure 3

SAM – PROCESS

Treatment: Alk. Cleaning, Acid Pickling, SAM-Treatment Painting; Substrate: AlMg1

Test Results	Two Layer Coil Coating Paint	One Layer PE-Powder Paint
Salt Spray Test ESS (4000 h)	< 1	< 1
Salt Spray Test CASS (1000 h)	< 1	1
Filiform Test (3000 h)	< 1	1
Outdoor Exposure (34 monts)	0	0
Cross Hatch Test (240 h constant humity)	-	Gt 0
T-Bend-Test T0/T1 [% paint adhesion]	≥ 95 / 100	-

Another group of products that are principally free of heavy metals are based on Silane chemistry. Fig. 4 gives an overlook on what products are available at present and where they can be used. The figure also summarizes test results obtained with silane coatings under paint.

Although some customers use these products already, the technology still under development and further improved products have to be worked out. Although there is still the risk of failure, we see the following advantages for the Silanes:

- heavy metal free,
- applicable to all standard metal surfaces,
- easy, if any, waste water treatment,
- can be used for passivation (without paint),
- paintable coatings

Figure 4. Commercial Products based on Silane Chemistry, Application and Test Results

OXSILAN	**Blank**	**Painted**	**Substrates**	SST **NSS 1008 h [mm]**	**ESS 1008 h [mm]**	**CASS 240 h [mm]**	**Cross hatch**
AL-500	X	X	Al		< 1		-
			Z	< 2			0
			CRS	≤ 2			0
MM-702		X	Al		< 1	0	0
			Z	< 1			0
			CRS	≤ 2			0
MM-705		X	Al		< 1		
			Z	< 2			0
			AZ	< 1			0
			ZA				
			CRS	≤ 2			0

On the other hand, the silane chemistry is complex and hydrolyzed silanes tend to react not only with the surface in question but also with each other or impurities which somehow get into the pretreatment bath. Thus, stability of bathes and concentrates are critical. And although paintability was proven in lab test, there is still the question to what extent silanes will interfere with subsequent painting stages in a paint shop.

To sum up this chapter, we conclude that there are new pretreatments on the market or under investigation that can not only replace chromating but may also result in considerable cost savings by optimizing processes andavoiding or minimizing waste and waste water treatment.

Precoated Substrates

Thin organic coatings with coating thickness of 1 to 5 µm have the potential to change the world of chemical pretreatment considerably. These coatings are usually applied by roll coating at the sheet manufactures, already, galvanizing in a coil coatingdirect application in galvanizing lines are being discussed. Most variants need a preceeding pretreatment step but there are some that provide pretreatment and protective coating at the same time. Such coatings were first introduced into the market in the early 90's with what we call Permanent Coatings. The first generation was chromate containing and was designed for the corrosion protection and anti-fingerprint coating of Galvalume. It was not meant to be painted although panting was possible especially with powder paints. Thus, a number of applications were founed mostly in the general industry, where customers used such precoated materials – e. g. Galfan – for the simplified manufacturing of white goods and the like. Pretreatment at the final customer consists of simple cleaning, and the finished good is powder painted, only.

Meanwhile, a second generation of such Permanent Coatings is being introduced into the market. The new products are chromium-free and corrosion protection is achieved by the use of nanoparticles. Fig. 5 summarizes test results with these new coatings. They not only provide excellent corrosion protection but possibly also better edge protection than the old products.

Figure 5. Gardobond Permanent-Coating - Cr-free - Product Program

Gardobond	Solids content	Application System	Substrate	Planned bath make up		Corrosion protection properties			
				Polymer component	Additive	Dry film coating w.	Salt spray test	VDA cycle test	Humidity cycle test
PC 4615	30 weight %	Chem-coater	AZ	99,0 weight % PC 4615	1,0 weight % GBA H 7409	1,5 – 2,0 g/m²	<5 % face corrosion after 480h	<5 % face corrosion after 20 cycles	n.a.
PC 4617	30 weight %	Chem-coater	Z ZA ZE	95,0 weight % PC 4617	5,0 weight % GBA H 7410	1,5 – 2,0 g/m²	< 5 % face corrosion after 360h	< 5 % face corrosion after 10 cycles	n.a.
PC 4619	30 weight %	Chem-coater	CRS	95,0 weight % PC 4619	5,0 weight % GBA H 7411	1,5 – 2,0 g/m²	n.a.	n.a.	< 5 % face corrosion after 20 cycles

The next product group, which was tried to be established in the market were the so-called Dry Lubricants. These are organic coatings formulated with an high amount of lubricating waxes. They were intended as substitutes for oils and greases in press shops. But although some advantages could be found, Dry Lubricants have not been used extensivly so far. Their main problem is that they need to be removed in the first cleaning stage of a pretreatment line thus giving rise to an enormous load of polymers and waxes which have to be removed by filtration means and causing high amounts of waste. The idea of dry lubricating may come up again, however, when the organic coating can remain in the surface and is overpainted in paint lines. The Permanent Coatings mentioned above contain waxes, already, to support roll forming operations.

The next step is pretreatment primers and especially welding primers that are on the market for several years and which will be substituted by a second generation of products in the very near future. The new generation of products again is chromium-free and at present they are intended to be used in automotive industry.

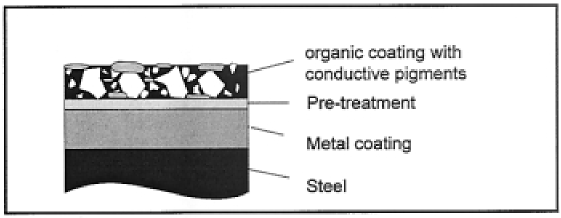
The requirements for welding primers are summarized in Fig. 6. The products contain electrocially conductive pigments such as zinc particles or iron phospide. Fig. 7 shows the coating structure. These coatings are suitable for subsequent electro-painting.

Figure 6. Requirements for Welding Primer

- Application via roll-coating in coil lines
- Good formability (ideally oil-free)
- Spot weldable (≥ 800 Spots, Welding area: 1,5 kA)
- E-coat paintability
- Highest Corrosion protection; no red rust after:
    1. Generation: 10 Cycle VDA-Test (Flange corrosion)
    2. Generation: 20 Cycle VDA-Test (Flange corrosion)
- Adhesive Bonding (Shear strength >20 MPa)
- Usable for bake hardening steel (T< 170°C)

Figure 7.

Welding Primer



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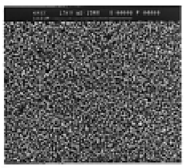

Fig. 8 summarizes the development of welding primers and also indicates what might come next: UV-cured welding primers. The advantage here is that even better cross linking is achieved and the coil manufacturer can apply the coating in the galvanizing line if he decides to invest in UV-lamps. Thus, he can avoid to transfer the coil to a coil coating line where at present the thermally cured welding primers are applied due to the necessary high curing temperature of 160 – 250 °C, depending on the product used.

Figure 8.

History of Welding Primers

Substrate	ZE	ZE	ZE Z	ZE Z	ZE Z
Pretreatment	Zn-ph, Cr CM Henkel	No-rinse, Cr CM Henkel	No-rinse, Cr-free CM Henkel 1456 PPG (Nupal)	No-rinse, Cr-free CM TP 10475 Henkel 1456	No-rinse, Cr-free CM TP 10475 Henkel 1456
Weldable Primer	1. Generation ~ 3 µm, 250°C pmt PPG Bonazinc	1. Generation ~ 3 µm, 250°C pmt PPG Bonazinc Henkel Granocoat	2. Generation ~ 6 µm, 160°C pmt PPG Bonazinc Henkel Granocoat CM/André BASF Akzo-Nobel	2+. Generation ~ 6 µm, 80°C pmt + UV CM/André	2++- Generation ~ 3 / 6 µm ? 160°C/250°C ? CM/André Henkel PPG BASF Akzo-Nobel

If such UV-curing stations are established, this will open the market for other type of products such as pretreatment primers that have excellent corrosion protection due to their highly cross linked organic matrix and that would have further advantages for the end user such as

- support of forming processes,
- coloured surfaces for easy visual inspection,
- excellent bare corrosion protection,
- paintability

It might even be possible to formulate coatings with self-healing capability. Such coatings would repair damages of a painted surface if they occur and moreover would provide an edge protection of a prepainted substrate thus opening up new potential for increased productivity at the end user.

Conclusion

As was shown in this paper, the suppliers of chemical pretreatment products strive to meet customers expections of environmentally more compatible products and of easy-to-handle and safe processes. At the same time, we understand ourselves as connecting link between metal producers, part manufacturers, and paint companies. Thus, we ensure that new pretreatment processes meet customer's demands.